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(54) **FLUORINATION PROCESS**

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#### FLUORINATION PROCESS

This invention relates to a method for producing pentafluoroethane. In a particular aspect, this invention relates to a method for fluorinating perhaloethylenes by the use of improved chromium fluorination catalysts.

The process provided by the present invention comprises contacting a vapor phase mixture comprising tetrachloroethylene and hydrogen fluoride with a chromium oxide ( $\text{Cr}_2\text{O}_3$ ) catalyst at a temperature between  $200^\circ\text{C}.$  and  $550^\circ\text{C}.$ , and recovering pentafluoroethane as product.

The present process is not limited to the conversion of tetrachloroethylene. Other perhaloethylenes such as 1,1-dichloro-2,2-difluoroethylene and chlorotrifluoroethylene can be fluorinated to pentafluoroethane by the process conditions of the present invention.

The process can be conducted either batchwise or continuously. In a preferred method, the reaction mixture is passed as vapor continuously over chromium oxide catalyst contained in a stainless steel or nickel-pipe reactor, and the effluent product gas is processed through a water scrubber and a drying unit, and then the product mixture is condensed and recovered. The components of the product mixture are conveniently separated by distillation.

The process temperature can vary between about  $200^\circ\text{C}.$  and  $550^\circ\text{C}.$ , with the preferred temperature range being between about  $300^\circ\text{C}.$  and  $400^\circ\text{C}.$  The process can be performed at pressures higher or lower than atmospheric pressure.



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The residence time of the feed mixture in the reaction zone varies widely depending on the reaction temperature and the composition of the feed mixture. The residence time will range from as low as 0.2 second at the higher temperatures to as high as three minutes or more at the lower temperatures. In a typical reaction sequence, the residence time of the feed material in the reactor will vary between about 0.5 second and 10 seconds at reaction temperatures between 300°C. and 400°C. The conversion of tetrachloroethylene proceeds rapidly and a high yield of pentafluoroethane can be obtained with a residence time of the order of 3 seconds at a temperature of 350°C. to 380°C. At temperatures above about 400°C. there is some loss of catalyst life and there is increased formation of by-products such as chloropentafluoroethane. Temperatures below about 300°C. have the disadvantage of slow reaction rates. The rate of gas flow can also be specified in terms of space velocity. In general, space velocities between 360 and 7200 liters per liter of catalyst per hour are suitable.

The mole ratio of hydrogen fluoride to tetrachloroethylene can vary broadly in the range between 1 and 10 moles of hydrogen fluoride per mole of tetrachloroethylene contained in the feed, with the preferred molar ratio being between 7 and 9 moles of hydrogen fluoride per mole of tetrachloroethylene. Additional hydrogen fluoride must be provided if the feed material contains other components which consume hydrogen fluoride. For example, in conducting the process chlorotetrafluoroethane and dichlorotrifluoro-

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ethane can be recovered as intermediate products from the product mixture and recycled as constituents of the feed material to be fluorinated so as to enhance the overall yield of pentafluoroethane.

The use of hydrogen fluoride in a ratio of between about 7 and 9 moles per mole of tetrachloroethylene suppresses the formation of partially fluorinated intermediates and by-products and permits the recovery of optimum yields of pentafluoroethane. If it is desirable to increase the production of partially fluorinated compounds such as trichlorodifluoroethane and tetrachlorofluoroethane, lower ratios of hydrogen fluoride are employed.

The chromium oxide catalyst of the process can be employed in several forms. The catalyst can be in the form of granular hydrous chromium oxide which is recovered as a precipitate formed by the action of ammonium hydroxide on an aqueous solution of a chromium salt such as chromium chloride, chromium nitrate, and the like. The same hydrous chromium oxide can be employed in the form of cubes prepared from the precipitate when it is in the form of a partially dried paste. In another variation, the hydrous chromium oxide can be mixed with a minor portion of chromium chloride and pelleted. The chromium chloride in the mixture performs as a lubricant to facilitate the pelleting operation. In another variation, chromium chloride and aluminum chloride can be coprecipitated with ammonium hydroxide. The resulting precipitate can be used in the form of granules, cubes or pellets as described above. In still another variation, the chromium oxide is

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employed on an alumina support. The preferred alumina supported chromium oxide catalysts are those prepared in the following manner. Porous alumina is impregnated with an aqueous solution of chromium trioxide. The material is then dried and reduced at elevated temperatures in an atmosphere of hydrogen. The catalyst so produced is particularly suitable in the practice of this invention. The porous alumina employed may be either alpha-alumina or the activated type such as chi-alumina, gamma-alumina, kappa-alumina, and the like.

To recover conveniently the product mixture produced by the process, the effluent gas is scrubbed with water, dried with a drying agent such as silica gel, activated alumina or a molecular sieve, and then the product mixture is condensed and recovered. The product mixture is fractionally distilled to separate pentafluoroethane from other components contained in the mixture. Partially fluorinated reaction products such as chlorotetrafluoroethane, dichlorotrifluoroethane, trichlorodifluoroethane and tetrachlorofluoroethane, can be retained as end-product if desired or recycled to the feed material to be further fluorinated to pentafluoroethane product.

Pentafluoroethane is valuable as a low-temperature refrigerant. The partially fluorinated products are of interest as solvents, refrigerants, aerosol propellants and as intermediates for resin monomers.

The following examples will serve to illustrate specific embodiments of the invention.

EXAMPLE 1

This example illustrates the preparation of chromium catalysts useful in the practice of this invention.

(a) Water (1145 milliliters) and ammonium hydroxide (588 grams, 28 per cent  $\text{NH}_3$ ) were placed in a flask equipped with a mechanical stirrer and a dropping funnel. A chromium chloride solution (520 grams of a 37 per cent chromic chloride solution and one liter of water) was added dropwise to the contents of the flask with stirring during a one-hour period. The resulting precipitate was separated from the supernatant liquid, and the precipitate was washed with water to remove ammonium chloride. The precipitate was then placed in a shallow pan and dried in a vacuum oven at  $70^\circ\text{C}$ . When the material was partially dried the paste was cut into small squares so that the hydrous chromium oxide ( $\text{Cr}_2\text{O}_3 \cdot x \text{H}_2\text{O}$ ) catalyst after complete drying was in the form of 1/4-inch cubes. The final drying of the hydrous chromium oxide catalyst was accomplished at a temperature of  $480^\circ\text{C}$ . under an atmosphere of nitrogen.

(b) Approximately 600 milliliters (247 grams) of hydrous chromium oxide prepared in the manner of section (a) above was mixed with 45 grams of anhydrous chromic chloride, and the mixture was ground in a ball mill for sixteen hours. The fine powder obtained was pelleted, employing 3/32-inch dies.

(c) Approximately 344 grams (2.5 moles) of aluminum chloride was dissolved in 1.5 liters of water. This solution was blended with a solution containing 395 grams (2.5 moles) of chromic chloride in 3.67 liters of water. The resulting solution was fed with vigorous agitation into a flask containing 920 grams of ammonium hydroxide (28 per cent  $\text{NH}_3$ ), diluted with 4 liters of water. The resulting precipitate was separated and washed several times with water. The material was transferred to shallow pans, cut into 1/4-inch cubes and dried in an oven at  $60^\circ\text{C}$ ., and then dried in a furnace at  $450^\circ\text{C}$ . for two days.

(d) Approximately 67.1 grams of chromium trioxide ( $\text{CrO}_3$ ) was dissolved in 102 grams of water. This solution was then added slowly with frequent agitation to 300 milliliters of Alcoa F-10 activated alumina (gamma-form, 6-8 mesh) contained in an evacuated flask. The material was partially dried by heating the flask under reduced pressure. It was then transferred to a one-inch i.d. nickel reactor and heated to  $200^\circ\text{C}$ . under a constant flow of nitrogen to complete the drying of the catalyst. The orange-red catalyst was then reduced with hydrogen for four hours at  $250^\circ\text{C}$ . to  $300^\circ\text{C}$ . to produce green colored chromic oxide ( $\text{Cr}_2\text{O}_3$ ) supported on gamma-alumina.

In a similar manner, a catalyst of chromium oxide supported on alpha-alumina was prepared. The alpha-alumina supported catalyst had the advantage of additional mechanical strength.



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(e) About 453 grams (1135 milliliters) of the hydrous chromic oxide prepared as above was placed in a two-inch i.d. nickel-pipe reactor and heated to 200°C. under a stream of nitrogen. Hydrogen chloride (24 liters/hour) was then passed over the catalyst and the temperature was increased to 350°C. to 360°C. This treatment was continued for a total of seventeen hours. The catalyst was ground to pass through a 30-mesh screen and was pelleted using 3/32-inch dies.

#### EXAMPLE 2

Over a 2.6 hour period, 835 grams of tetrachloroethylene and 168 grams of hydrogen fluoride were vaporized over a 250 milliliter volume of granular hydrous chromium oxide catalyst [similar to the catalyst described in Example 1, section (e)] at a temperature of 350°C. to 380°C. in a one-inch i.d. nickel reactor. The effluent from the reactor was passed through a water scrubber and a calcium chloride tower, and was collected in dry ice-cooled traps. Distillation of the condensate product (543 grams) yielded 59 grams of pentafluoroethane, boiling point -48°C., which was identified by mass spectral analysis. Other products isolated from the reaction mixture included chlorotetrafluoroethane (boiling point -10°C.), dichlorotrifluoroethane (boiling point 28°C.), and small amounts of chloropentafluoroethane (boiling point -38°C.) and dichlorotetrafluoroethane (boiling point 4°C.).

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EXAMPLE 3

During a 1.3 hour period, 125 grams of 1,1-dichloro-2,2-difluoroethylene and 85 grams of hydrogen fluoride were vaporized over a 180 milliliter volume of pelleted hydrous chromium oxide catalyst [similar to the catalyst described in Example 1, section (b)] at a temperature of 350°C. to 360°C. in a one-inch i.d. nickel reactor. The effluent from the reactor was passed through a water scrubber, a calcium chloride tower, and was collected in dry ice-cooled traps. Distillation of the condensate mixture yielded 33 grams of pentafluoroethane (boiling point -48°C.) and 29 grams of chlorotetrafluoroethane (boiling point -10°C.).

EXAMPLE 4

Over a three hour period, 430 grams of chlorotri-fluoroethylene and 227 grams of hydrogen fluoride were vaporized over a 160 milliliter volume of pelleted hydrous chromium oxide catalyst [similar to the catalyst described in Example 1, section (b)] at a temperature of 350°C. to 400°C. in a one-inch i.d. nickel reactor. The reaction products were scrubbed and recovered in traps as in the previous examples. Distillation of the condensate mixture yielded approximately 130 grams of pentafluoroethane, 94 grams of chlorotetrafluoroethane, 162 grams of unreacted chlorotri-fluoroethylene, and small amounts of chloropentafluoroethane and dichlorotetrafluoroethane.

WHAT IS CLAIMED IS:

1. A process which comprises contacting, in the vapor phase, hydrogen fluoride with a compound selected from the group consisting of perchlorofluoroethylene and tetrachloroethylene with a hydrous chromium oxide catalyst at a temperature between 200°C. and 550°C., and recovering pentafluoroethane as product.

2. A process which comprises contacting a vapor phase mixture comprising hydrogen fluoride and perchlorofluoroethylene with a hydrous chromium oxide catalyst at a temperature between 200°C. and 550°C., and recovering pentafluoroethane as product.

3. A process which comprises contacting a vapor phase mixture comprising hydrogen fluoride and tetrachloroethylene with a hydrous chromium oxide catalyst at a temperature between 200°C. and 550°C., and recovering pentafluoroethane as product.

4. A process which comprises contacting a vapor phase mixture comprising hydrogen fluoride and tetrachloroethylene in a molar ratio between 1 and 10 with a hydrous chromium oxide catalyst at a temperature between 200°C. and 550°C. and recovering pentafluoroethane, chlorotetrafluoroethane and dichlorotrifluoroethane as products.

5. A process which comprises contacting a vapor phase mixture comprising hydrogen fluoride and tetrachloroethylene in a molar ratio between 1 and 10 with a hydrous chromium oxide catalyst at a temperature between 200°C. and 550°C., separating pentafluoroethane as product, and recycling chlorotetrafluoroethane and dichlorotrifluoroethane to feed mixture.



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